Quantification of tin and lead in binary alloys using voltammetry of immobilized microparticles

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Abstract

Voltammetry of immobilized microparticles (VMP) has been used in this work for the quantitative determination of tin and lead particles in their binary alloys. Carbon paste electrodes, which contained small amounts of tin and lead or their mixtures, were used as working electrodes and square wave voltammograms of each electrode were recorded. Quantification was performed using optimum experimental conditions, obtained by an experimental design technique. The calibration was made by measuring the percentage peak height of each metal taking the sum of peak currents of the both metals as 100 %. The results were compared with quantitative results of X-ray fluorescence (XRF) technique to evaluate the capability of VMP method in its quantitative determination of solid samples.

Key words: voltammetry of immobilized microparticles, square wave voltammetry, carbon paste electrode, central composite design, tin, lead.

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1. Introduction

Abrasive stripping voltammetry (AbSV), also known as voltammetry of immobilized microparticles (VMP) is a simple, fast and cheap electrochemical technique first described by F. Scholz in the late 1980's [1, 2]. It is a very versatile tool used for solid-state characterization [3, 4]. In brief, a micro-sample is transferred by abrasion to the surface of a paraffin impregnated graphite electrode (PIGE) or a carbon paste electrode (CPE). This is then analysed using voltammetric techniques.

In heritage science, VMP has received particular attention in the analysis of mural and oil paintings, textiles, ceramic materials and glasses, metals and alloys [5 and references therein] because of its ability to assess the state of conservation, and detect degradation products prior to intervention. Recent VMP-based investigations have focused on the examination of metallic heritage, the study of corrosion and the identification of corrosion products [6-8].

In addition several methods have been reported which allow the quantification of material using VMP. They include the use of percentage currents [9], charge values [10-12], internal standards [13], the standard addition method [14] and the use of Tafel plots [15]. Previous work in our research group involved the quantification of Cu, Sn, Pb and Zn in their copper based binary, ternary and quaternary alloys. Here, the

percentage of the oxidation current for each metal, which is directly related to the ratio of the metal in the binary matrices, was employed for the calibration [16].

In this paper the aim is to examine this technique for lead-tin alloys. Tin-lead alloys are used in the manufacturing of organ pipes. The pipes that produce the diapason tones of organs generally are made of alloys with tin contents varying from 20 to 90 % according to the tone required. In comparison to our previous work [16], here we make use of square wave voltammetry instead of differential pulse voltammetry as it shows a better sensitivity and reproducibility. Fast scanning of applied potential range (higher scan rates) is another advantage of this technique. In brief, this work consists three parts. The first part examines the type of electrolyte which is suitable to identify the elements tin and lead. Here the aim is to acquire in which electrolyte the two elements can be measured simultaneously without seeing any overlap in their current peaks. The second experiment focuses on optimizing the measurement conditions with the aim of having the current peaks well separated. Here an experimental design approach based on the central composite design (CCD) is used to investigate the effect of the scan rate and concentration of the electrolyte on the oxidation potentials of tin and lead. Finally the two elements are being quantified in their binary mixtures and in two real samples.

2. Experimental

2.1. Apparatus

The VMP measurements were performed using an Autolab Eco Chemie potentiostat (PGSTAT 10) in a three electrode cell with a Ag/AgCl/KCl (sat) reference electrode and a graphite wire as auxiliary electrode. The working electrode was a carbon paste electrode, 5 mm in diameter and 85 mm in length. All measurements were performed using square wave voltammetry in a potential window between -1.50 V to -0.5 V.

2.2. Reagents

Solid paraffin, acetic acid, sodium hydroxide, sodium nitrate, sodium chloride, oxalic acid and ammonium dichromate were purchased from Merck. Potassium dichromate, ammonium carbonate, ammonium acetate, ammonium persulfate, tri-ammonium orthophosphate, tin, and lead powders were purchased from Aldrich and graphite powder (≤ 0.1 mm) was obtained from Fluka. All reagents were of analytical grade.

2.3. Procedure for the fabrication of the carbon paste electrodes

All carbon paste electrodes were fabricated using the same conditions. Graphite (≤ 0.1 mm) and paraffin were mixed in a ratio of 60:40 (w/ w) to prepare the carbon paste. A total amount of 130 mg of the solid carbon paste was transferred into a crucible and then the solid sample to be studied was added to the crucible. The crucible was placed inside an oven (~ 100 ^{o}C) for 5 minutes. After this step the liquid paste containing the solid sample was mixed well to prepare a homogeneous mixture. After a few minutes at room temperature the carbon paste was solid again and ready to use. The paste was then packed into a

plastic tubing body with a length of 20 mm and a width of 5 mm diameter. Electrical contact was made by a copper rod with a length of 75 mm connected to one side of the carbon paste. The electrode was polished after each measurement using a clean paper sheet to renew its surface.

2.4. Experimental design

To optimize the experimental conditions an experimental design strategy called "Central Composite Design" or "Response Surface Design" was used. The aim of the optimization step is to obtain a maximum separation between the tin and lead oxidation peaks. The design allows a simultaneous variation of all experimental factors and distinguishes possible interactions amongst them, which is not detectable with classical optimization methods. This approach also decreases the number of experiments required [17].

The variables considered in the current optimization process were the scan rate (50 - 460 mV/s) and the concentration of the electrolyte (0.01 – 2 M). The scan rate was chosen as variable as it is directly linked to the frequency and step potential. In this work a step potential of 5.1 mV and an amplitude of 19.95 mV and therefore a frequency range of ≥ 40 mV/s were applied and this range of the scan rate was optimized.

The polynomial equations, response surface and central design for a particular response were obtained using the statistical software package Essential Regression 97 [18]. For an experimental design with two factors, the model includes linear, quadratic, and cross terms and can be expressed by Equation 1:

$$\text{Response} = b_0+b_1\times F_1+b_2\times F_2+b_3\times F_1\times F_1+b_4\times F_2\times F_2+b_5\times F_1\times F_2 \qquad \text{(Eq 1)}$$

Where F_1 and/F_2 are the variable parameters, and b_0 through b_5 are the coefficient values obtained through a multivariate linear regression. b_0 indicates the intercept and in error calculation has been used. The statistical significance of the predicted model was evaluated by an analysis of variance (ANOVA) and least square techniques. Replicates (n=4) of the central points were performed to estimate the experimental error.

3. Results and Discussion

3.1. Electrochemical behaviour of tin and lead in different electrolytes

Carbon paste electrodes containing tin, lead and a mixture of them were prepared and square wave voltammograms of each electrode were recorded in 10 different electrolytes. The electrolytes are listed in Table 1 together with the obtained results, which demonstrate that the only common electrolyte in which the two metals can be determined is sodium hydroxide. For all other electrolytes the peaks overlap.

3.2. Optimization

To obtain the maximum separation between the current peaks and to overcome any interference between them, the concentration of the electrolyte (sodium hydroxide) and the scan rate were optimized using the central composite design. Table 2 shows the list of experiments and the levels of the coded values including the corresponding response of each experiment. Figure 1 shows the p-values, obtained from the

ANOVA. In statistical analyses p-values are the most commonly used tool to measure evidence against a hypothesis model. The p-value is a probability, with a value ranging from zero to one, which shows the chance of observing a difference between the real value and the estimated value. The p-values show that the sodium hydroxide concentration (F_2) is the most significant factor. Another significant interaction term is ($b_4 \times F_2 \times F_2$).

The corresponding 3D response surface and contour plots are shown in Figure 2. They show the prominent effect of the scan rate (F_1) as well as the sodium hydroxide concentration (F_2) on the response ($|\Delta E|$). The optimum conditions were selected using the surface plot, which shows that the separation between the tin and lead oxidation peaks is maximum when a scan rate between 254.4 – 356.7 mV/s and a sodium hydroxide concentration of 0.9 – 1.1 M is used. In the rest of this work we will use a scan rate of 260 mV/s and sodium hydroxide concentration of 1 M as optimal values.

Figure 3 shows a good separation between the tin and lead current peaks using the optimal scan rate and sodium hydroxide concentration. Even though a higher scan rate tends to result in a higher sensitivity, Figure 3 shows that it simultaneously decreases the separation between the peaks, resulting in wide peaks with a higher base line.

3.3. Quantification procedure of tin-lead alloy

3.3.1. Calibration

The ratio of both anodic oxidation signals was used for the quantification of the tin-lead alloys. Carbon paste electrodes of tin and lead mixture were made in different compositions and a square wave voltammogram of each electrode was recorded using the optimal conditions obtained above. Each experiment was repeated at least 5 times therefore, the percentages of the currents which have been used in the calibration plots are the average of 5 measurements. The correlation between the oxidation currents of tin (I_{Sn}) and lead (I_{Pb}) and the percentage of current for these metals in their binary mixtures (I %) is [10]:

$$I_{Sn}(\%) = \frac{I_{Sn}}{I_{Sn} + I_{Pb}} \times 100$$

$$I_{Pb}(\%) = \frac{I_{Pb}}{I_{Sn} + I_{Pb}} \times 100 \qquad \text{(Eq 2)}$$

Figure 4 shows the data as a function the composition of the mixture (Sn and Pb plotted separately) together with a linear regression (regression coefficient $0.98 \leq R^2$).

3.3.2. Prediction

To test the capability of the calibration plots for predicting tin and lead amounts in their mixtures, two electrodes of tin-lead mixture for each calibration plot were made and using the same procedure the amounts of metals, which had been added to the electrodes were predicted.

Each measurement was replicated 3 times. The results are shown in Table 3. In this work we have obtained relative standard deviations of the order of 2.42 to 13.16, which falls within the expectations [20].

3.3.3. Analysis of tin-lead alloy (real sample)

The method described above was used for identification and also quantification of tin and lead in two real binary alloys with different compositions (Sn 5% / Pb 95% and Sn 15% / Pb 85%). The experimental conditions were the optimal conditions. For each alloy small amounts of the sample (40 mg) were used to make a carbon paste electrode and square wave voltammograms of the samples were recorded. Each alloy was measured four times. Using the obtained calibration plots for tin and lead, the amounts of each metal in the alloys were predicted. To compare the capability of the VMP method in quantification with other techniques the alloys were also analyzed by X-ray fluorescence spectroscopy (XRF). The later was chosen, as it is a strong analytical technique used for routine, relatively non-destructive chemical analyses and is typically used for bulk analyses. The results are shown in Figure 5 and demonstrate no significant difference between the VMP and XRF results.

4. Conclusions

Voltammetry of microparticles using a carbon paste electrode was used for the identification and quantification of tin and lead in their binary alloys. The effect of different electrolytes and other variables such as scan rate and electrolyte concentration were studied using an experimental design method. This allowed us to optimize the measurement conditions leading to voltammograms with clearly resolved peaks. The second part of the paper dealt with the quantification of the metals in powder mixtures, but also in real binary alloys and gave satisfactory results. The results confirm that VMP is a useful and cost effective technique to qualitative as well as quantitative studies of metals/alloys.

5. Acknowledgements

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Table 1. Different electrolytes used to identify Sn, Pb in their binary mixtures.

Electrolyte (0.1 M)	**Tin and lead peaks**
Sodium hydroxide	*separated*
Oxalic acid	overlap
Sodium nitrate	overlap
Acetic acid	overlap
Sodium chloride	overlap
Potassium dichromate	overlap
Ammonium carbonate	overlap
Ammonium acetate	overlap
Ammonium dichromate	overlap
Triammonium orthophosphate	overlap

Table 2. Design matrix and relative $|\Delta E|$ values in central composite design for two factors: scan rate (mV/s) and sodium hydroxide concentration (M). The factors are expressed in coded values.

Exp. #	**F_1 – Scan rate (mV/s)**	**F_2 – [NaOH] (M)**	**I∆EI (mV)**
1	2	0	246.8
2	-1.41	1.41	206.6
3$^{(R)}$	0	0	221.5
4	-2	0	181.3
5	1.41	-1.41	251.7
6$^{(R)}$	0	0	256.8
7$^{(R)}$	0	0	241.6
8	-1.41	-1.41	216.5
9	0	2	251.8
10	1.41	1.41	261.9
11$^{(R)}$	0	0	261.9
12	0	-2	65.4
Coded value (-2)	50	0.01	-
Coded value (-1.41)	70	0.3	-
Coded value (0)	230	1	-
Coded value (+1.41)	440	1.41	-
Coded value (+2)	510	2	-

(R): Replicated experiment. (n=4)

Table 3. The predicted amounts of tin and lead and their standard deviations and relative standard deviations.

Metal	Sample # 1* (mg)	Sample # 2* (mg)	Std $_{(Sample\ \#\ 1)}$	Std $_{(Sample\ \#\ 2)}$	RSD% $_{(Sample\ \#\ 1)}$	RSD% $_{(Sample\ \#\ 2)}$
Tin	Added: 12 Found: 12.28	Added: 27 Found: 27.23	0.48	0.65	4.33	2.50
Lead	Added: 20 Found: 19.75	Added: 5 Found: 4.80	0.52	0.67	2.42	13.16

*Replicated: 5 times

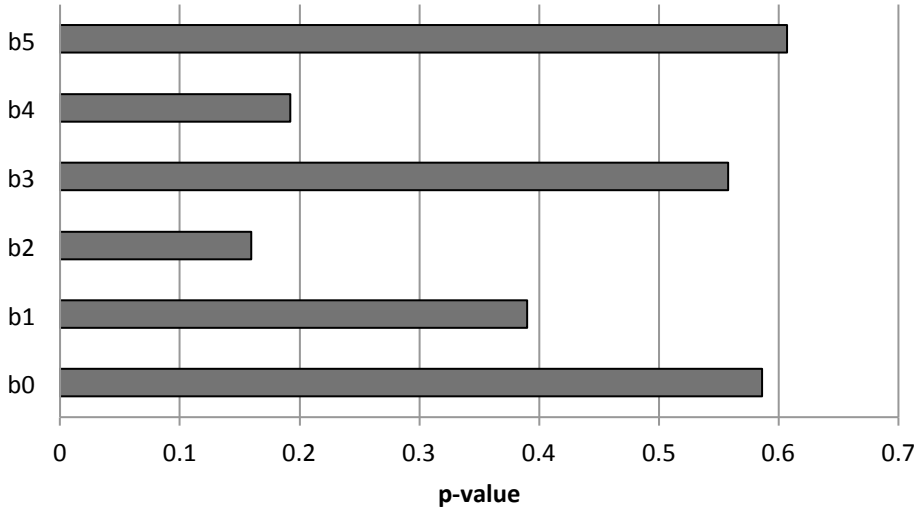
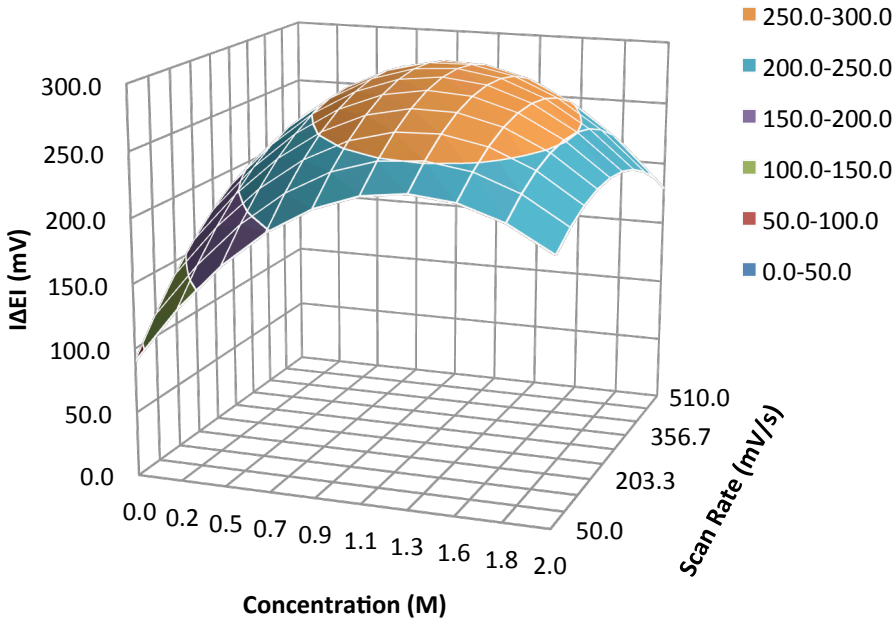
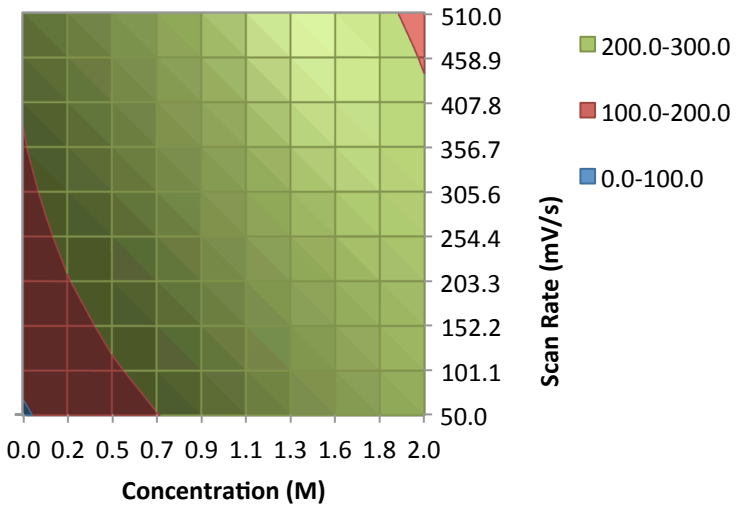


Figure. 1. Obtained p-values.



(A)



(B)

Figure. 2. Response surface (A) and contour plot (B) estimated from the central composite design by plotting scan rate as a function of sodium hydroxide concentration.

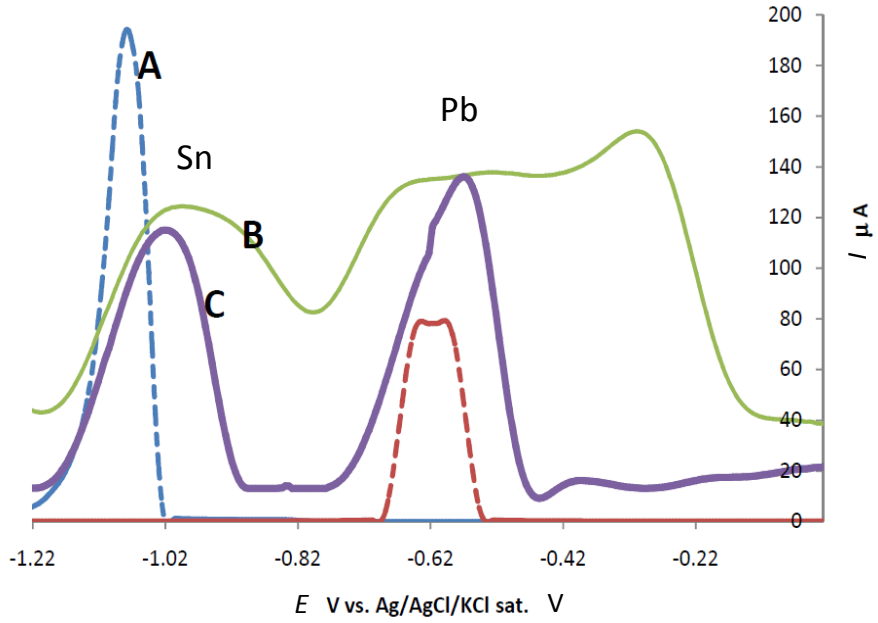


Figure. 3. Square wave voltammograms of tin and lead in sodium hydroxide solution. (A – dotted line) tin and lead single electrodes, concentration sodium hydroxide 1 M, scan rate 260 mV/s (optimum conditions). (B – thin full line) tin and lead mixture electrode, concentration sodium hydroxide 0.1 M, scan rate 408 mV/s. (C – thick full line) tin and lead mixture electrode, concentration sodium hydroxide 1 M, scan rate 260 mV/s, frequency 51 Hz, step potential 5.1 mV, amplitude: 19.95 mV (optimum conditions).

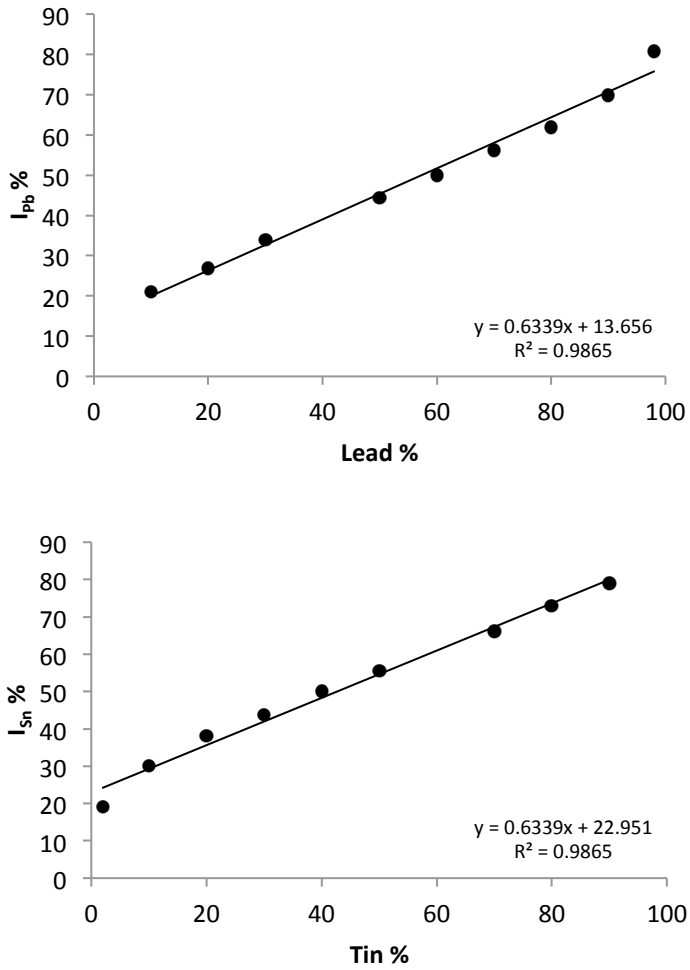


Figure 4. Dependence of tin and lead oxidation peak current percentages on the composition of the tin-lead alloy (total amount of the sample: 40 mg).

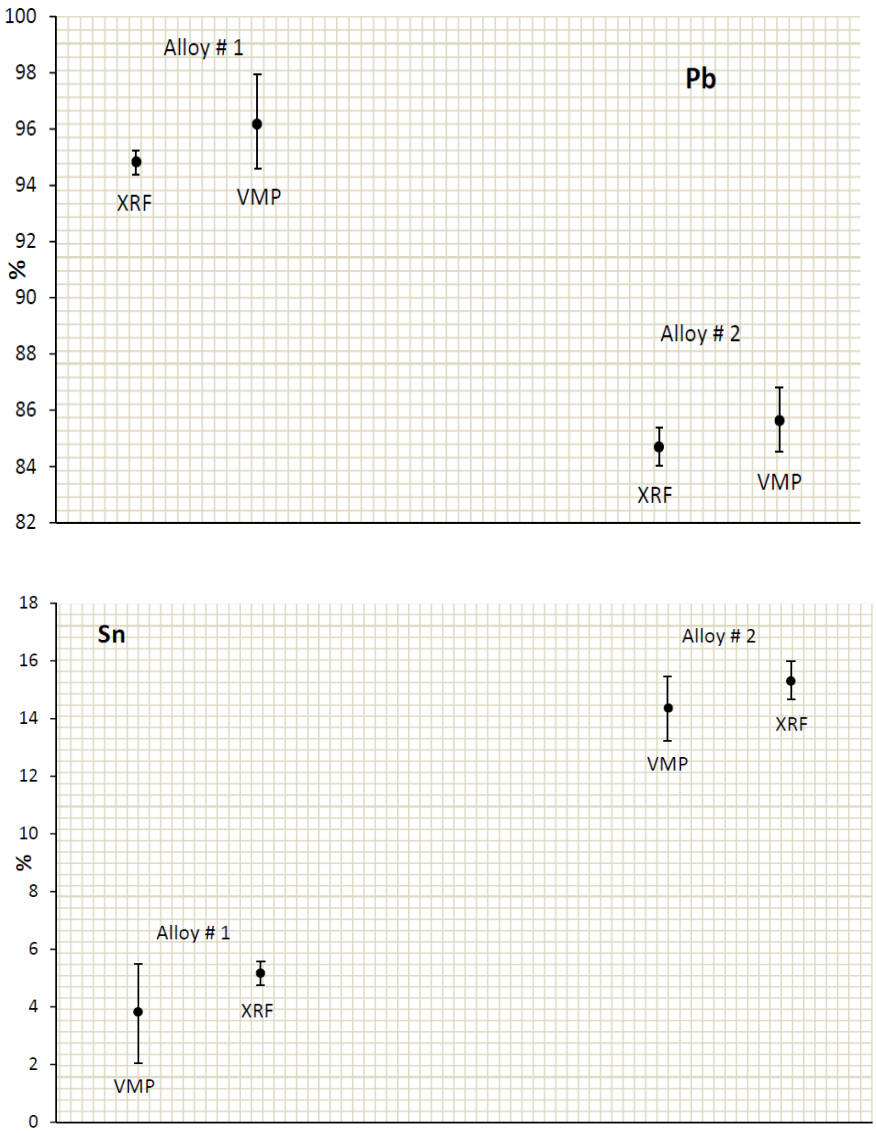


Figure 5. The estimated amounts of tin and lead in their binary alloys using tin-lead calibration plots (total amount of the sample: 40 mg). The composition of the two alloys has also been analyzed by XRF. Replicated: 4 times (VMP) and 3 times (XRF).